AD-781 623

# DETERMINING THE VAPOR PRESSURE OF METALS AT HIGH TEMPERATURES

V. M. Amonenko, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

17 June 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

UNCLASSIFIED
Security Classification

AD781623

## DOCUMENT CONTROL DATA - R & D

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

| | |
|---|---|
| 1. ORIGINATING ACTIVITY (Corporate author)<br>Foreign Technology Division<br>Air Force Systems Command<br>U. S. Air Force | 2a. REPORT SECURITY CLASSIFICATION<br>UNCLASSIFIED<br>2b. GROUP |

3. REPORT TITLE

DETERMINING THE VAPOR PRESSURE OF METALS AT HIGH TEMPERATURES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Translation

5. AUTHOR(S) (First name, middle initial, last name)

V. M. Amonenko, V. Ye. Ivanov, et al

| | | |
|---|---|---|
| 6. REPORT DATE<br>1966 | 7a. TOTAL NO. OF PAGES<br>14 | 7b. NO. OF REFS<br>11 |

| | |
|---|---|
| 8a. CONTRACT OR GRANT NO.<br>b. PROJECT NO.<br>c.<br>d. | 9a. ORIGINATOR'S REPORT NUMBER(S)<br>FTD-HT-23-887-74<br>9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) |

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

| | |
|---|---|
| 11. SUPPLEMENTARY NOTES<br>Reproduced from best available copy. | 12. SPONSORING MILITARY ACTIVITY<br>Foreign Technology Division<br>Wright-Patterson AFB, Ohio |

13. ABSTRACT

20, 11

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

FTD-HT- 23-887-74

# EDITED TRANSLATION

FTD-HT-23-887-74 17 June 1974

DETERMINING THE VAPOR PRESSURE OF METALS AT HIGH TEMPERATURES

By: V. M. Amonenko, V. Ye. Ivanov, et al

English pages: 9

Source: Eksperimental'naya Tekhnika i Metody Vysokotemperaturnykh Izmereniy, 1966, pp. 85-90

Country of Origin: USSR
Translated by: MSgt Victor Mesenzeff
Requester: FTD/PDTI
Approved for public release;
distribution Unlimited.

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

## U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

| Block | Italic | Transliteration | Block | Italic | Transliteration |
|---|---|---|---|---|---|
| А а | *А а* | A, a | Р р | *Р р* | R, r |
| Б б | *Б б* | B, b | С с | *С с* | S, s |
| В в | *В в* | V, v | Т т | *Т т* | T, t |
| Г г | *Г г* | G, g | У у | *У у* | U, u |
| Д д | *Д д* | D, d | Ф ф | *Ф ф* | F, f |
| Е е | *Е е* | Ye, ye; E, e* | Х х | *Х х* | Kh, kh |
| Ж ж | *Ж ж* | Zh, zh | Ц ц | *Ц ц* | Ts, ts |
| З з | *З з* | Z, z | Ч ч | *Ч ч* | Ch, ch |
| И и | *И и* | I, i | Ш ш | *Ш ш* | Sh, sh |
| Й й | *Й й* | Y, y | Щ щ | *Щ щ* | Shch, shch |
| К к | *К к* | K, k | Ъ ъ | *Ъ ъ* | " |
| Л л | *Л л* | L, l | Ы ы | *Ы ы* | Y, y |
| М м | *М м* | M, m | Ь ь | *Ь ь* | ' |
| Н н | *Н н* | N, n | Э э | *Э э* | E, e |
| О о | *О о* | O, o | Ю ю | *Ю ю* | Yu, yu |
| П п | *П п* | P, p | Я я | *Я я* | Ya, ya |

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

## FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

| Russian | English |
|---|---|
| sin | sin |
| cos | cos |
| tg | tan |
| ctg | cot |
| sec | sec |
| cosec | csc |
| sh | sinh |
| ch | cosh |
| th | tanh |
| cth | coth |
| sch | sech |
| csch | csch |
| arc sin | sin$^{-1}$ |
| arc cos | cos$^{-1}$ |
| arc tg | tan$^{-1}$ |
| arc ctg | cot$^{-1}$ |
| arc sec | sec$^{-1}$ |
| arc cosec | csc$^{-1}$ |
| arc sh | sinh$^{-1}$ |
| arc ch | cosh$^{-1}$ |
| arc th | tanh$^{-1}$ |
| arc cth | coth$^{-1}$ |
| arc sch | sech$^{-1}$ |
| arc csch | csch$^{-1}$ |

---

| Russian | English |
|---|---|
| rot | curl |
| lg | log |

# DETERMINING THE VAPOR PRESSURE OF METALS AT HIGH TEMPERATURES

V. M. Amonenko, V. Ye. Ivanov,
G. P. Kovtun, V. S. Pavlov, and
A. A. Kruglykh

Basically two methods are used to study the vapor pressure of metals: evaporation from an open surface and effusion [1, 2, 3]. Each of these methods has its own limitations. Due to the fact that the emissivities of many substances are unknown and can vary during evaporation, the use of the Langmuir method is quite often difficult. In the Knudsen method these difficulties are eliminated, since it is not necessary to know the effective evaporation surface and evaporation coefficient $\alpha$ does not enter into calculations. However, difficulties arise in the latter method when manufacturing high-temperature chambers for the evaporation of refractory materials. The small dimensions of the effusion opening of the cell at low vapor pressure of the studied substance require longer time to carry out the test. The effusion method can change into that of evaporation from an open surface by increasing the dimensions of the opening and decreasing the height of the effusion chamber walls. Earlier, a number of authors have established a mathematical dependence of the evaporation rate on the geometrical dimensions of the evaporator and the evaporation coefficient [4, 5, 6]. The obtained relationships are cumbersome and their practical application for calculations is difficult.

Examining the chamber for the evaporation as a successive connection of its individual elements, it is possible in vacuum technology to derive a general formula using the vacuum anology [7]. In this case the corrective coefficients can be expressed by the Clausing probability [8].

In this work the vapor pressure of refractory metals was determined using the evaporation rate of a substance from a cylindrical crucible. The use of such a crucible for determining the evaporation rate has a number of advantages: there are no special requirements imposed on the structure of the surface of the evaporated substance, the temperature can be determined by an optical device without introducing corrections for the emissivity coefficient of the substance, since emission from the crucible in the first approximation can be considered as absolutely black. The duration of the test in determining the evaporation of the substance from such a crucible is considerably shorter than during the evaporation from an effusion cell.

The crucible with metal on the bottom can be considered as a system consisting of a vapor source and a cylindrical tube connected with it in sequence. The walls of the crucible create certain resistence against the efflux of vapor molecules. For such a system it is possible to calculate the nature of the flow and intensity of the vapor flow through the outlet opening of a cylindrical tube.

For a round tube with length $l$ and diameter d the probability that the molecule will traverse distance $l>0$ is equal to

$$W=\frac{1}{1+f(l/d)}, \qquad (1)$$

where $f(l/d)$ - certain function which is determined by the dimensions of the tube and which satisfies the conditions

$$f(l/d)\rightarrow 0 \text{ when } l\rightarrow 0,$$
$$f(l/d)\rightarrow \infty \text{ when } l\rightarrow \infty.$$

Total conductivity of the cylindrical crucible is equal to

$$\frac{1}{F_1}=\frac{1}{F_2}+\frac{1}{F_3}, \tag{2}$$

where $F_1$, $F_2$, and $F_3$ - conductivities (total, of the surface, and of the tube, respectively). The conductivity of a round tube with length $l$ and diameter d

$$F_3=S\sqrt{\frac{RT}{2\pi M}}\cdot\frac{1}{f(l\,d)}, \tag{3}$$

where S - cross-section area of the tube; T - absolute temperature; R - universal gas constant; M - molecular weight.

$$F_2=\alpha S\sqrt{\frac{RT}{2\pi M}}. \tag{4}$$

In this case the effect of the evaporation coefficient is equivalent to the decrease in the evaporation surface.

Total conductivity of the cruicble

$$\frac{1}{F_1}=\frac{1}{S\sqrt{\frac{RT}{2\pi M}}}\cdot\left[\frac{1}{\alpha}+f(l/d)\right]. \tag{5}$$

From expression (1) we find $f(l/d)$ =

$$f(l/d)=\frac{1-W}{W}.$$

Values W for round tubes of varied diameter were calculated with considerable accuracy by Clausing and are equal to

$$W=\frac{1}{1+0{,}5l/r} \text{ when } l/r<1{,}5,$$

$$W=\frac{1+0{,}4\,l/r}{1+0{,}95l/r+0{,}15\,(l/r)^2} \text{ when } l/r>1{,}5,$$

where r - tube radius.

The expression for total conductivity of the cylindrical crucible with the consideration of (6) can be written as

$$\frac{1}{F_1}=\frac{1}{S\sqrt{\frac{RT}{2\pi M}}}\cdot\left[\frac{1}{\alpha}+\frac{1}{W}-1\right]. \qquad (7)$$

The conductivity of the system can be expressed in terms of vapor pressure using the equation of gas state

$$PV=\frac{G}{M}\cdot RT. \qquad (8)$$

Dividing both sides of equation (8) by $P_2-P_1$, we obtain the expression for the conductivity in the usual form

$$F_1=\frac{PV}{P_2-P_1}=\frac{GRT}{M}\cdot\frac{1}{P_2-P_1}. \qquad (9)$$

In this case $P_1=0$, since evaporation occurs in a vacuum; $P_2=P$, i.e., vapor pressure at temperature T. Then we obtain

$$F_1=\frac{G}{P}\cdot\frac{RT}{M}. \qquad (10)$$

Substituting into this expression for $F_1$ from (7), we obtain

$$P=\frac{G}{S}\left(\frac{1}{\alpha}+\frac{1}{W}-1\right)\sqrt{\frac{2\pi RT}{M}}, \qquad (11)$$

where G - evaporation rate, in $g\cdot s^{-1}$; S - area of the outlet opening; α - evaporation coefficient; W - Clausing coefficient.

To calculate the vapor pressure by formula (11), it is necessary to know the evaporation coefficient α.

If one is to evaporate a metal from cylindrical crucibles with different ratios $l/d$ (i.e., with different coefficients of W) at the same temperature, it is possible to determine the numerical value of the evaporation coefficient α.

$$P = \frac{G_1}{S_1}\left(\frac{1}{\alpha} + \frac{1}{W_1} - 1\right)\sqrt{\frac{2\pi RT}{M}}, \tag{12}$$

$$P = \frac{G_2}{S_2}\left(\frac{1}{\alpha} + \frac{1}{W_2} - 1\right)\sqrt{\frac{2\pi RT}{M}}; \tag{13}$$

solving equations (12) and (13) with respect to α, we obtain

$$\alpha = \frac{\frac{G_1}{S_1} - \frac{G_2}{S_2}}{\frac{G_2}{S_2}\left(\frac{1}{W_2} - 1\right) - \frac{G_1}{S_1}\left(\frac{1}{W_1} - 1\right)}. \tag{14}$$

The obtained equations (11) and (14) enable us to calculate the vapor pressure and the evaporation coefficient.

To confirm the validity of these conclusions we measured the vapor pressure of silver in the 800-960° range. The tests were carried out on a vacuum installation consisting of a vacuum chamber, trap cooled by liquid nitrogen, and the diffusion and backing pumps. The use of the trap with liquid nitrogen prevents the oil from the pump system to enter the working chamber and affords the possibility to work in vacuum $5-7 \cdot 10^{-7}$ mm Hg.

High temperature resistance furnace was used to heat the crucibles (the number of tungsten spirals and the distance between them was selected experimentally in order to obtain the necessary temperature distribution).

The temperature was measured by an optical pyrometer through a glass window. A corresponding correction for the absorption in the glass was introduced into the pyrometer readings.

The dependence of vapor pressure on temperature is shown in figure 1 and is expressed by the equation

$$\lg P\,(\text{мм}) = -\frac{14030}{T} + 8{,}8860.$$

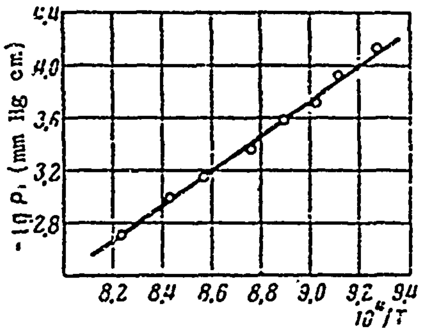

Figure 1. Vapor pressure of silver as a function of temperature.

The evaporation coefficient of silver, calculated by formula (14), proved to be equal to 0.15.

These results are in good agreement with the data in literature [5, 9].

Let us examine some extreme cases which can occur in practice depending on the numerical values of the evaporation coefficient $\alpha$ which enters formula (11). Such cases can be: 1) very low evaporation coefficient values, i.e., large values of $1/\alpha$; 2) high values of $l/d$, i.e., cases when relatively long crucibles are used with not very low values of the evaporation coefficient.

With very low values of $\alpha$ the following inequality is valid:

$$\frac{1}{\alpha} \gg \frac{1}{W} - 1, \tag{15}$$

and formula (11) assumes the following form:

$$P = \frac{G}{\alpha S}\sqrt{\frac{2\pi RT}{M}}. \tag{16}$$

Thus, a case is possible which is similar to the evaporation with an open surface and, consequently, to calculate the vapor pressure it is necessary to know the value of evaporation coefficient $\alpha$.

In a second case, with relatively large ratios of length of the crucible to the diameter, in the factor $\left(\frac{1}{W}-1+\frac{1}{\alpha}\right)$ we can disregard the term $\left(\frac{1}{\alpha}-1\right)$ which characterizes the surface properties of the evaporating substance as compared with the term 1/W which is a function of geometrical dimensions. Apparently, in this case, it is not necessary to know the numerical value of the evaporation coefficient and the pressure of the saturated vapor will be determined by the expression

$$P=\frac{G}{S\cdot W}\sqrt{\frac{2\pi RT}{M}}. \qquad (17)$$

The last formula coincides with the expression used for determining the vapor pressure by the effusion method when evaporation originates from the chamber with an opening of finite thickness, which is characterized by the presence of the Clausing coefficient W.

To find out at what values of $l/d$

$$\frac{1}{W}\gg\frac{1}{\alpha}-1, \qquad (18)$$

we can use equation (17). To determine the vapor pressure we studied the evaporation rate as a function of the ratio of length of the crucible to the diameter for silver ($\alpha$=0.15) and chromium ($\alpha$=0.5) [5, 10].

Silver and chromium were evaporated from molybdenum crucibles with the various ratios of length to the diameter. The results of the experiment have shown that, beginning with ratio $l/d$ completely defined for each metal, the sublimation rate at constant temperature changes insignificantly. This ratio is different for silver and chromium, which is explained by the difference in the evaporation coefficients of these metals.

For the various metals whose evaporation coefficients are different and do not equal to unity there is a ratio $l/d$ with which inequality (18) is satisfied with a sufficient degree of accuracy and, consequently, the vapor pressure is determined by expression (17). For chromium this ratio is equal to 8.5, which corresponds to the inequality of type $\frac{1}{0.13}>>\frac{1}{0.5}-1$ or 8>1, i.e., in practical application, inequality 10>1 must be satisfied. In a general case the ratio and the value of inequality $\frac{1}{W}>>\frac{1}{\alpha}-1$ will be determined by the accuracy of the procedure. For an additional confirmation of these conclusions we measured the vapor pressure of solid chromium obtained using the vacuum distillation method [11] in the 1,200-1,350° range. The design of the isothermic furnace has enabled us to carry out evaporation simulataneously, using two cylindrical crucibles with the ratio $l/d$ equalling 8.5 and 4.5. The sublimation rate was determined by the formula

$$m_x=\left[\frac{1}{W}-1+\frac{1}{\alpha}\right]m \text{ for } l/d=4.5,$$

$$m_x=\frac{1}{W}\cdot m \text{ for } l/d=8,5,$$

where m - sublimation rate without the consideration of the crucible conductivity.

The measurement results for the evaporation rate of chromium from long and short crucibles, presented in the table, are in good agreement with one another within the experimental errors.

Sublimation rate of chromium (in g$\cdot$cm$^2$/s)

| Temp.. in °C | Long crucible | Short crucible |
|---|---|---|
| 1180 | $2.8\cdot10^{-6}$ | $2,75\cdot10^{-6}$ |
| 1205 | 4.68 | 4,56 |
| 1220 | 7,06 | 7,05 |
| 1250 | $1,40\cdot10^{-5}$ | $1,30\cdot10^{-5}$ |
| 1270 | 2,12 | 2.20 |
| 1280 | 2,85 | 3,03 |
| 1315 | 5,02 | 5,10 |
| 1350 | $1,01\cdot10^{-4}$ | — |

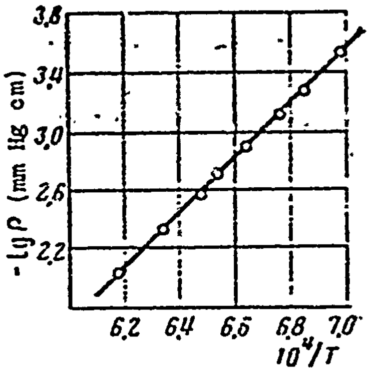

Figure 2. Vapor pressure of chromium as a function of temperature.

The evaporation coefficient of chromium, calculated by formula (14), is equal to 0.5. Thus, for chromium, condition (18) is virtually fulfilled when $l/d=7.8$. Figure 2 shows the chromium vapor pressure as a function of temperature, calculated using the rate of sublimation from a crucible with the ratio $l/d=8.5$. In processing the experimental data using the method of least squares, we obtained the equation for the chromium vapor pressure in the 1,200-1,350° range

$$\lg P\,(\text{мм}) = 10{,}890 - \frac{20830}{T}.$$

The obtained equation is in good agreement with the literature data.

BIBLIOGRAPHY

1. M. Knudsen. Ann. Physik., 1909. 29, 179.
2. I. Langmuir. Phys. Rev., 1913, 2, 239.
3. R. Speiser, H. Johnston. Trans. ASM. 1950, 42, 238.
4. G. L. Whitman. J. Chem. Phys.. 1952. 20, 161.
5. M. G. Rossman, I. Jarwood. B. I. Appl. Phys., 1954. 5, 7.
6. Ю. Н. Любитов, В. М. Полянский. Докл. АН СССР, 1959, 125, № 1, 135.
7. С. П. Детков. 1957. ЖФХ, 31. 2367.
8. P. Clausing. Ann. Physik., 1911, 130, 389.
9. Ан. Н. Несмеянов. 1959. ЖФХ, 33. 341.
10. Ан. Н. Несмеянов, Дё Дык Ман. Докл. АН СССР, 1959, 116, 330.
11. В. М. Амоненко, А. А. Круглых, Г. Ф. Тихинский. ФММ, 1959, 7, 86.